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Structure and Properties of Polymer Interphases

F. James Boerio
Department of Materials Science and Engineering
University of Cincinnati
Cincinnati, Ohio 45221

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<p>The effect of metal substrates on the molecular structure of γ-aminopropyltriethoxysilane (γ-APS) primers during drying at elevated temperatures was determined using infrared spectroscopy. When drying was carried out at 110°C, the amino groups in primer films formed on 2024 aluminum and copper were oxidized to form imine groups but those in films formed on iron, titanium, and 1100 aluminum were not. When drying was carried out at 150°C, the films formed on iron, copper, titanium, and 2024 aluminum were oxidized to form imine structures but films formed on 1100 aluminum were not. These results indicate that copper-containing substrates catalyzed oxidation of the primer but the oxide on 1100 aluminum, which contained no copper, inhibited the free-radical oxidation.</p> <p>The molecular structure of interphases between model adhesive systems and metal substrates was determined by using x-ray photoelectron spectroscopy and infrared spectroscopy to characterize the fracture surfaces of adhesive joints prepared by curing beams of epoxies against metal beams. The structure of the interphase depended strongly on the curing agent, metal</p>				
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- When an epoxy was cured against primed substrates using an anhydride curing agent, the anhydride reacted with the amino groups of the primer to form amide and imide groups. Very close to the interface, carboxylate ions formed by reaction of the anhydride with the substrate. When an anhydride/epoxy was cured against unprimed copper, the anhydride etched the oxide, forming carboxylate species that diffused into the adhesive. When the same adhesive was cured against aluminum, the anhydride adsorbed onto the oxide to form a surface carboxylate but the oxide was not etched.

The use of surface-enhanced Raman scattering (SERS) for non-destructive characterization of interphases between polymers and metals was demonstrated. When a thick film of acrylic adhesive was cured against a silver substrate and examined using SERS, a strong Raman spectrum attributed to a metal salt of saccharin, a component of the adhesive cure system, was observed but no evidence of Raman scattering by the bulk adhesive was observed. It was concluded that saccharin segregated to the metal surface, forming a salt, and that SERS could be used to characterize polymer/metal interphases without interference from normal Raman scattering by the bulk of the polymer as long as the polymer film was less than approximately 1,000 Å in thickness.

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I. Introduction

A great deal of progress has been made in recent years in understanding the importance of the surface properties of the substrate in obtaining strong, durable adhesive bonds to metals. Adhesive bonds to aluminum provide an interesting case in point. Hydration of the oxide to pseudoboehmite is usually considered responsible for the failure of most adhesive bonds to aluminum during exposure to warm, moist environments (1). Anodizing aluminum in phosphoric acid provides a porous oxide that is very resistant to hydration in warm water (2). The resistance of the anodic oxide to hydration is due to the formation of a thin film of AlPO_4 on the outer surface and is essential for durability (3). The porosity of the oxide is important in determining the joint strength since it facilitates mechanical interlocking between the adhesive and the substrate. Somewhat similar results have been obtained for titanium anodized in chromic acid (4).

One aspect of adhesive joints that is not very well understood concerns the structure and properties of polymer "interphases." Interphases represent the transition regions between polymer/substrate interfaces and the bulk of the polymer. It is usually assumed that the molecular structure and properties of the interphase are the same as those of the bulk polymer. However, chemical and physical processes are influenced by interfaces and there may be a gradation of properties as the interface is approached but the extent of those structural gradations and their depth away from the interface and into the polymer are not well known.

Since the interphase is responsible for transferring the stress from one adherend to another in adhesive joints and is frequently the site of environmental attack, it is essential to develop techniques for controlling and characterizing the molecular structure of interphases in adhesive joints. However, few investigations concerned with the molecular structure of interphases in adhesive joints or composites have been reported.

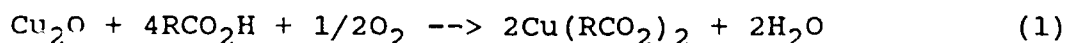
Some time ago, Kumins (5) suggested that the mobility of a polymer in contact with a solid was different from that of the bulk polymer due to the adsorption of polymer segments onto the surface of the solid. Kwei (6) subsequently suggested that the effects of adsorption onto a filler particle could extend as far as 1500 Å into a polymer.

More recently, Carter et al (7) investigated the surface chemical effects between electrogalvanized steel (EGS) and low carbon steel (LCS) adherends bonded with an epoxy adhesive cured with dicyandiamide. They found that lap joints made with EGS adherends were more durable than joints made with LCS adherends during cyclic corrosion testing. Reflection-absorption infrared spectra obtained from steel, zinc, and zinc oxide substrates coated with the epoxy/dicyandiamide adhesive deposited from dimethylformamide solution illustrated the influence of substrate composition on the interfacial molecular structure. Carter suggested that a redox reaction between metallic zinc and dicyandiamide resulted in formation of a unique molecular species in the interphase. However, no reaction was noted between zinc oxide and dicyandiamide. It was concluded that zinc was oxidized

and dicyandiamide was reduced when dicyandiamide was cured against metallic zinc.

Kim (8) investigated adhesive joints prepared by curing polyimide films on copper substrates at 400°C. Using transmission electron microscopy (TEM), Kim showed that copper-rich particles were distributed in the polymer matrix 80 to 200 μm away from the interface. It was suggested that the polyamic acid reacted with the oxidized copper surface during the cure cycle, producing the particles. When copper was deposited on polyimide, the results were considerably different and a sharp interface was obtained. The peel strength of joints prepared by curing polyimide against copper (73 g/mm) and those of joints prepared by depositing copper on cured polyimide (5 g/mm) correlated with the interphase morphologies.

Allara (9-11) investigated the degradation of polyethylene cured against copper as a model for polyolefin-insulated cable. Results obtained from reflection-absorption infrared spectroscopy showed that oxidation of polyethylene was catalyzed by the copper surface. The susceptibility of polyolefin/copper laminates to enhanced oxidation depended on the rate of dissolution of copper ions from the oxidized copper surface and their concentration within the polymer matrix. Allara showed that the formation of a copper salt at the interface could be described by the reaction



where RCO_2H is an acid formed as a result of primary oxidation of the hydrocarbon chain. These salts diffused up to several

thousand angstroms into the polyethylene matrix after heating for several thousand hours at temperatures ranging from 40° to 87°C.

Crompton (12) used transmission electron microscopy (TEM) to determine the morphological features of the interphase formed when an epoxy adhesive was cured against aluminum. A transition region between the interface and the bulk of the adhesive was observed in which the physical and chemical properties of the adhesive differed from those of the bulk. Two types of transition layers were observed. The first extended up to a micron from the interface. The other extended only about 100 Å. Pretreatment of the substrate prior to bonding appeared to have little effect on the formation of the transition layers. However, Crompton did not determine the molecular structure of the interphases he observed.

Prior to this work, few investigations of interphases involving silane coupling agents had been reported. However, Garton (13, 14) used attenuated total reflection infrared spectroscopy (ATR) to characterize the molecular structure of an anhydride/epoxy adhesive cured against a germanium crystal primed with an aminosilane coupling agent. He found that the amino groups of the silane reacted with the anhydride to produce amides but found no evidence of imide formation.

The primary objective of this research was to determine the structure of interphases formed when selected model adhesive systems were cured against metal substrates. Substrates that were considered included aluminum, copper, iron, and titanium. In some cases the substrates were pretreated with an aminosilane

primer while in other cases the substrates were left untreated. It was found that copper-containing substrates catalyzed the oxidative degradation of the aminosilane primer but that commercially pure aluminum substrates inhibited the oxidation. The characteristics of the interphases formed when model adhesives were cured against primed substrates varied depending on the adhesive. Thus, when an epoxy/tertiary amine adhesive was cured against a primed substrate, there was little interdiffusion of the adhesive and primer and a sharp interface between the adhesive and primer was obtained. However, when an epoxy/anhydride adhesive was cured against a primed substrate, there was considerable diffusion of the curing agent into the primer and a broad interphase with unique composition was formed. When an epoxy/polyamine adhesive was cured against unprimed aluminum, the amino groups adjacent to the surface were protonated while those in the bulk of the adhesive were not and the extent of cure of the adhesive was greater at the surface than in the bulk. Finally, when the epoxy/anhydride adhesive was cured against unprimed substrates, the anhydride reacted with the oxide to form carboxylate species. In the case of copper substrates, the oxide was etched and the carboxylates diffused into the adhesive. However, the anhydride adsorbed onto oxidized aluminum substrates to form a monolayer of surface carboxylates but the oxide was not etched.

An additional objective was to develop non-destructive methods for characterizing interphases. Surface-enhanced Raman scattering was found to be very useful for such purposes and was

used to show that acidic compounds were adsorbed from anaerobic acrylic adhesives onto metal substrates to form salts.

II. Experimental

Sheets of titanium-6 Al, 4V, oxygen-free, high conductivity (OFHC) copper, and low carbon steel were obtained from Timet, Inc., AMAX Copper, Inc., and Armco, Inc., respectively. 1100 and 2024 aluminum were purchased from commercial suppliers. Coupons (1/8 x 2 x 3") were cut from the sheets and mechanically polished to a mirror finish using standard metallographic techniques. The coupons were ground on a series of dry corundum papers with grit sizes ranging from 350 through 600 and then polished on cloths with 15 mm alumina abrasive slurries. Aluminum coupons were given a final polish to a mirror finish using 3.0 μm MgO slurries. Titanium, steel, and copper substrates were polished to a mirror finish using a series of alumina slurries with particle sizes ranging from 0.3 to 0.05 μm . After the polishing was completed, the mirrors were rinsed several times in distilled, deionized water, blown dry with nitrogen, and examined using reflection-absorption infrared spectroscopy (RAIR).

Primer films were applied by immersing the mirrors into 1 or 2% aqueous solutions of γ -aminopropyltriethoxysilane (γ -APS) (A-1100, Union Carbide) at pH 10.4 for one minute, blowing the excess solution off the mirrors using a strong stream of nitrogen, and allowing the films to dry at room temperature. After drying for thirty minutes, the primer films on the mirrors were examined using RAIR. The mirrors were then placed into an

oven and the films were dried in air at an elevated temperature for an additional hour before being re-examined using RAIR.

Reactivity of silane primer films with respect to epoxy resins (Epon 828, Shell Chemical Co.) was determined by applying γ -APS films to polished metal mirrors as described above and allowing the films to dry at room temperature for thirty minutes. The mirrors were then placed in a shallow container filled with epoxy resin, and the container was placed into an oven which had been pre-heated to the desired temperature. After one hour, the mirrors were removed from the oven, rinsed repeatedly with methylethylketone (MEK) to remove unreacted epoxy, and examined using RAIR.

Substrates for double cantilever beams (DCB) were machined from 2024-T3 aluminum and 1018 steel barstock to a final size of 0.25 x 0.50 x 7.50", degreased with acetone, and then metallographically polished.

Initial polishing of the substrates was with a series of dry silicon carbide abrasive papers ranging from 240 to 600 grit. After the surfaces were ground, they were wet polished on microcloths (Beuhler, Inc) with a 14 μm alumina slurry and either a 0.3 μm alumina slurry for the steel samples or 3.0 μm magnesia slurry for aluminum samples. Finally, the substrates were rinsed in distilled deionized water and blown dry with nitrogen.

Some of the substrates were pretreated by being immersed in 1% aqueous solutions of γ -APS at pH 10.4 for 1 minute, withdrawn, and blown dry with a stream of nitrogen gas. The resulting primer films, which were about 100 Å in thickness as measured by

ellipsometry, were allowed to polymerize in the lab atmosphere at room temperature for 30 minutes before the adhesive was cast.

Three adhesive systems were considered. One consisted of the epoxy resin Epon 828 cured with ten parts per hundred of triethylamine (TETA, Fisher Scientific Co.). Another consisted of Epon 828 cured with a tertiary amine (DMP-30, Shell Chemical Co.) in a 100:6 ratio by weight. The third adhesive system consisted of Epon 828 cured with nadic methyl anhydride and the accelerator benzyldimethylamine (NMA and BDMA, respectively, Fisher Scientific Co.), in a 100:100:2 ratio by weight. The epoxy resin was usually preheated to 60°C prior to addition of the curing agent and, if appropriate, accelerator.

DCB samples were produced by clamping an aluminum mold lined with sheets of fluorocarbon plastic around the polished adherend and casting the warm adhesive into the mold (see Figure 1). The entire assembly was then placed in an oven and cured at preselected temperatures and times. A chromel-alumel thermocouple was placed near the adherend/adhesive interface to monitor exotherms. After curing, the samples were removed from the mold and allowed to cool to room temperature overnight.

Due to differences in thermal expansion coefficients of the epoxy and the substrate, residual stresses at the interface were sufficient for cracks to be propagated very close to the interface. Sections two inches long were cut from the adhesive and adherend failure surfaces and analyzed using x-ray photoelectron (XPS), attenuated total reflection infrared (ATR), and reflection-absorption infrared (RAIR) spectroscopies.

In some cases, miniature double cantilever beam (MDCB) samples were prepared by clamping a similar aluminum mold around a smaller polished adherend (0.5" x 0.75") and casting the adhesive into the mold. The mold was placed in an oven and the adhesive was cured at various temperatures and times. The samples were allowed to cool overnight to room temperature, removed from the mold, and end-milled to reduce the adhesive thickness to 0.063". The samples were fractured by immersion into liquid nitrogen and placed directly into the sample chamber of the infrared spectrophotometer. After the infrared spectroscopy was completed, the samples were placed into the test chamber of the XPS system for analysis.

Infrared spectra were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared spectrophotometer and external reflection accessories provided by Harrick Scientific. RAIR spectra were obtained using one reflection at an angle of 78° . 50 scans at 4.0 cm^{-1} resolution were averaged to obtain the spectra. Unless otherwise stated, the spectra reported are actually difference spectra obtained by subtracting spectra of clean polished substrates from spectra of sample surfaces. ATR spectra of the adhesive failure surfaces were obtained by pressing the surfaces against germanium ATR crystals. The angle of incidence was 45° .

XPS spectra of the failure surfaces were obtained using a Perkin-Elmer Model 5300 ESCA System. K_{α} radiation from a magnesium anode at a power of 300 watts was used to excite the

spectra. Pass energy was 44.74 eV for survey spectra and 17.89 eV for multiplex spectra.

III. Results and Discussion

A. Effect of Metals on the Molecular Structure of Aminosilanes.

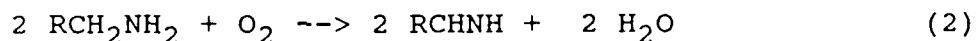
Aminosilane primer films applied to steel and titanium substrates were characterized by a strong band near 1120 cm^{-1} and by weaker bands near 920, 1040, 1330, 1470, 1570, and 1640 cm^{-1} (see Figure 2A). The band near 920 cm^{-1} was assigned to SiOH groups while those near 1040 and 1120 cm^{-1} were assigned to SiOSi groups, showing that the silane was hydrolyzed in solution and then polymerized on the surface. The bands near 1330, 1470, 1570, and 1640 cm^{-1} were assigned to amine bicarbonates formed by absorption of carbon dioxide from the atmosphere (15, 16).

When the as-formed films were dried in air at 110°C for one hour, several changes were observed in the spectra (see Figure 2B). The band near 1120 cm^{-1} shifted upward to about 1150 cm^{-1} , the shoulder near 1040 cm^{-1} became well resolved, and the band near 920 cm^{-1} decreased in intensity due to increased polymerization in the films. The bands near 1330, 1470, 1570, and 1640 cm^{-1} all decreased in intensity, indicating that the bicarbonates were mostly dissociated by heating at 110°C .

Essentially identical results were obtained when γ -APS films were formed on titanium and 1100 aluminum substrates and then dried at 110°C . However, the results obtained for 2024 aluminum substrates were somewhat different. As-formed films were characterized by a strong, broad band near 1100 cm^{-1} and by weaker bands near 890, 1330, 1470, 1570, and 1640 cm^{-1} (see

Figure 3A). The bands near 890 and 1100 cm^{-1} were attributed to SiOH and SiOSi groups, respectively, while those near 1330, 1470, 1570, and 1640 cm^{-1} were again related to amine bicarbonates. The frequencies of the bands due to SiOH and SiOSi groups were lower for 2024 aluminum substrates than for steel and titanium substrates, indicating less polymerization of the silane, perhaps due to hydrogen bonding between silanol groups and hydroxyl groups on the oxidized surface of the aluminum.

After the as-formed films on 2024 aluminum were dried at 110 $^{\circ}\text{C}$ for one hour, the spectrum shown in Figure 3B was obtained. The shape of the band near 1100 cm^{-1} remained the same, showing that little additional polymerization occurred. Bands due to the bicarbonate disappeared and were replaced by bands near 1600 and 1660 cm^{-1} . The band near 1660 cm^{-1} was related to the C=N stretching mode of an imine formed by the oxidation of the amine:



Similar results were obtained for copper substrates.

When these experiments were repeated at a drying temperature of 150 $^{\circ}\text{C}$, interesting results were obtained. The infrared spectra of the films formed on iron, titanium, and 2024 aluminum were very similar and consisted of bands near 1040 and 1150 cm^{-1} due to SiOSi groups and near 1660 cm^{-1} due to imines (see, for example, Figure 4). The bands near 1330, 1470, 1570, and 1640 cm^{-1} due to bicarbonates were not observed and neither was the band near 1600 cm^{-1} . However, the bands due to bicarbonates were definitely observed in spectra of γ -APS films that were formed on

1100 aluminum and then dried at 150°C for one hour but the band near 1660 cm⁻¹ was relatively weak (see Figure 5).

These results show that oxidation of the amine to the imine is favored when γ -APS films formed on 2024 aluminum are dried at 110°C but not when films formed on iron, titanium, or 1100 aluminum are. The difference between the behavior of γ -APS films on 2024 aluminum and other substrates was attributed to catalysis of the oxidation reaction by copper, which is present in 2024 aluminum as an alloying element at a concentration of about 4.5%.

When as-formed films were dried at 150°C for one hour, extensive oxidation of the amine to the imine was observed on iron, titanium, and 2024 aluminum substrates but very little imine formation was observed for γ -APS films formed on 1100 aluminum. These results indicate that the oxidation proceeds quickly at 150°C without catalysis and that the lack of oxidation for the γ -APS films formed on 1100 aluminum during drying at 150°C is related to oxidation inhibition by the surface oxide.

Additional experiments were carried out to determine if the oxidation of the amino groups to imine groups was likely to occur during curing of adhesive joints and to determine if such oxidation would inhibit the reaction between a silane primer and an epoxy adhesive cured against a primed substrate. γ -APS primers were applied to iron and 2024 aluminum mirrors as described above. The mirrors were immersed in shallow containers filled with epoxy resin and the containers were placed in an oven that was preheated to either 75 or 150°C. After one hour, the mirrors were removed from the containers, rinsed several times

with MEK to remove unreacted epoxy, and then examined using infrared spectroscopy.

When the reaction between the epoxy and the silane film formed on iron and 2024 aluminum was carried out at 75°C, the bicarbonates were not dissociated and there was little reaction between the epoxy and the silane. Infrared spectra obtained from the mirrors after rinsing in MEK clearly showed the bands near 1330, 1470, 1570, and 1640 cm^{-1} that were related to the bicarbonates but only a weak band characteristic of epoxies was observed near 1510 cm^{-1} , showing that little epoxy was retained on the mirrors.

When the reaction between the epoxy and γ -APS films formed on iron was carried out at 150°C, the results were much different. Little evidence of the bands near 1330, 1470, 1570, and 1640 cm^{-1} was observed in the infrared spectra from the mirrors after rinsing, showing that the bicarbonates had dissociated and only a weak band due to the imine was observed near 1660 cm^{-1} . At the same time, several bands characteristic of the epoxy, including those near 1605, 1510, and 1260 cm^{-1} were seen, demonstrating that there was considerable reaction between the silane and the epoxy and that a significant amount of epoxy was retained on the mirrors after rinsing (see Figure 6).

However, when infrared spectra were obtained from the primer films on 2024 aluminum after reaction with the epoxy at 150°C for one hour and rinsing, different results were found. The band near 1660 cm^{-1} was observed but those near 1330, 1470, 1570, and 1640 cm^{-1} were not, showing that the bicarbonates were

dissociated. From the intensity of the band near 1660 cm^{-1} , it was evident that significant oxidation of the amine to the imine had occurred. The band near 1510 cm^{-1} was weak, implying that there was little reaction between the silane and the epoxy and that there was little retained epoxy.

B. Molecular Structure of Epoxy/Silane Interphases.

The RAIR spectrum from the adherend fracture surface of a DCB prepared using the epoxy/tertiary amine adhesive cast on a primed 1018 steel substrate and cured for 2 hours at 75°C , was dominated by a strong band near 1120 cm^{-1} and weaker bands near 1040, 1330, 1470, 1570 and 1640 cm^{-1} (see Figure 7). As indicated above, these bands were all related to the aminosilane primer containing absorbed carbon dioxide. Only a very weak band characteristic of epoxies was observed near 1510 cm^{-1} . The bicarbonates did not dissociate during cure, thereby blocking the amino groups and preventing reaction between adhesive and primer.

When the curing reaction was carried out at 150°C for one hour, the RAIR spectrum obtained from the adherend failure surface was significantly different (see Figure 8A). Several bands associated with the epoxy were seen near 1605, 1510, 1260, and 830 cm^{-1} . However, the intensity of these bands obscured the bands of the underlying interphase. In order to obtain spectra of the interphase, the spectrum of the epoxy was removed through the use of digital subtraction using the 1510 cm^{-1} band of the adhesive for normalization.

When DCB samples were prepared as described above using the epoxy/tertiary amine adhesive and unprimed substrates, complete

interfacial failure always occurred and it was not possible to obtain the RAIR spectrum of the adhesive on the metal substrate. Therefore, an RAIR spectrum was obtained from a thin film of the epoxy/tertiary amine that was cast on a 1018 steel substrate from a dilute solution in MEK and cured for 1 hour (see Figure 8B) and subtracted from the spectrum in Figure 8A to obtain the spectrum of the interphase (see Figure 8C).

The spectrum in Figure 8C clearly showed the siloxane bands at 1040 and 1150 cm^{-1} . The latter band was shifted upward about 30 cm^{-1} relative to the 1120 cm^{-1} band in Figure 7, indicating increased polymerization of the primer at the higher curing temperatures. The weaker band near 1660 cm^{-1} was due to the C=N stretching mode of imine groups formed by oxidation of the amino groups in the primer. The negative band near 1740 cm^{-1} was due to a C=O stretching vibration resulting from oxidation of the thin adhesive film cured against the steel substrate (see Figure 8B). The interphase in these specimens consisted of a highly crosslinked siloxane network in which some amino groups were oxidized to imines but there was no evidence of unusual primer-adhesive interactions.

In DCB specimens prepared from primed substrates, failure occasionally occurred near the metal/primer interface. RAIR spectra from the adherend failure surfaces showed little retained adhesive. In order to characterize the interphase in such specimens, the adhesive failure surfaces were examined. Figure 9A shows the ATR spectrum obtained from the adhesive failure surface of a DCB specimen prepared using the epoxy/tertiary amine

adhesive cast on a primed 1018 steel substrate and cured at 150°C for one hour. As expected, strong bands near 1605, 1510, 1260, and 830 cm^{-1} associated with the epoxy phase again obscured the spectrum of the interphase. Therefore, the ATR spectrum of the adhesive failure surface of a similar specimen prepared using an unprimed substrate (see Figure 9B) was obtained and subtracted from the spectrum in Figure 9A to obtain the spectrum of the interphase shown in Figure 9C. As usual, the 1510 cm^{-1} band was used to normalize the two spectra. The difference spectrum showed the siloxane bands near 1040 and 1150 cm^{-1} in addition to the imine band near 1660 cm^{-1} . This spectrum closely resembles the RAIR spectrum taken from the adherend side (see Figure 8C).

The RAIR spectrum obtained from the adherend failure surface of a DCB sample prepared using a primed aluminum substrate and the epoxy/anhydride adhesive is shown in Figure 10A. Bands near 1510 and 1730 cm^{-1} were characteristic of the cured adhesive.

The RAIR spectrum of a thin film of the adhesive applied to an aluminum substrate from an MEK solution and cured is shown in Figure 10B. The band near 1730 cm^{-1} was due to the C=O stretching mode of ester groups produced by the reaction between the anhydride and the epoxy.

The RAIR spectrum of the adherend failure surface from a DCB sample prepared using an unprimed aluminum substrate is shown in Figure 10C. The broad band near 1000 cm^{-1} was an envelope of bands due to oxidation products on the aluminum surface including Al_2O_3 . The bands near 1600 and 1450 cm^{-1} were related to

carboxylate vibrations due to salt formation between the curing agent and the aluminum.

Figure 10D is the difference spectrum obtained by removing the spectra of the adhesive (Figure 10B) and the substrate (Figure 10C) from the spectrum of the adherend failure surface (Figure 10A) and represents the interphase. Subtraction of the adhesive spectrum was based on the intensity of the band near 1730 cm^{-1} while subtraction of the substrate was based on the intensity of the broad band near 1000 cm^{-1} .

The spectrum of the interphase (Figure 10D) shows bands near 1650 and 1550 cm^{-1} characteristic of amide formation. The small band near 1700 cm^{-1} is due to the C=O vibration of a cyclic imide. The sharp peak near 1780 cm^{-1} is the C=O vibration from residual anhydride groups. The two bands near 1150 and 1040 cm^{-1} are the SiOSi vibrations from the siloxane network. The interphase region in this case contains amides, imides, residual unreacted curing agent and a crosslinked siloxane network.

C. Structure of Metal/Anhydride-Cured Epoxy Interphases.

RAIR spectra obtained from the adherend failure surfaces of MDCB specimens prepared with the epoxy/anhydride adhesive and 2024 aluminum and copper substrates are shown in Figure 11. Spectra obtained from the aluminum substrates were characterized by bands near 1609 , 1460 , and 960 cm^{-1} . The intense band near 960 cm^{-1} was assigned to a vibration of the oxide while the bands near 1609 and 1460 cm^{-1} were assigned to the asymmetric and symmetric stretching modes of carboxylate groups, respectively. The RAIR spectrum obtained from the adherend failure surface of a

MDCB sample with a copper substrate was characterized by bands near 1570 and 1420 cm^{-1} that were also attributed to carboxylate stretching vibrations. However, little evidence of the oxide Cu_2O was noted due to the absence of a band near 645 cm^{-1} .

XPS multiplex spectra shown in Figure 12 were obtained from the failure surfaces of copper/epoxy MDCB specimens. $\text{C}(1s)$ spectra from the adherend failure surface contained three components near 284.6, 286.3, and 288.1 eV which were attributed to hydrocarbon, carbon singly bonded to oxygen, and carbon in a metal carboxylate, respectively (see Figure 12A). One $\text{Cu}(2p_{3/2})$ photoelectron line was observed near 932.8 eV in multiplex spectra of the adherend failure surface but two lines were observed with kinetic energies near 918.0 eV and 916.6 eV in the $\text{Cu}(\text{LVV})$ Auger spectra.

In order to identify the copper species, the modified Auger parameter (α') was calculated. This parameter is defined as

$$\alpha' = h\nu + \text{BE}_p - \text{BE}_a \quad (3)$$

where $h\nu$ is the energy of the x-ray photons, BE_a is the apparent binding energy of the Auger electrons, and BE_p is the binding energy of the photoelectrons. This equation can be rewritten as

$$\alpha' = \text{KE}_a + \text{BE}_p \quad (4)$$

where KE_a is the kinetic energy of the Auger electrons. Since chemical shifts for the Auger electrons are sometimes more pronounced than those of the photoelectron lines, use of the modified Auger parameter as well as the photoelectron binding energy can be useful in chemical state identification.

The values of the modified Auger parameter (α') calculated from the $\text{Cu}(2p_{3/2})$ electron binding energy and the $\text{Cu}(\text{LVV})$ Auger electron kinetic energies observed in the spectra shown in Figure 12A were 1850.8 and 1849.4 eV and were characteristic of metallic copper and Cu_2O , respectively (17, 18). No evidence of the copper/NMA salt was observed in the $\text{Cu}(2p_{3/2})$ or $\text{Cu}(\text{LVV})$ spectra. However, since the $\text{C}(1s)$ multiplex spectra and the RAIR spectra (see Figure 11B) indicated the presence of a small amount of the salt, it was likely that bands in the Auger spectra associated with the copper salt were obscured by the intense bands near kinetic energies of 916.6 and 918.0 eV.

The $\text{C}(1s)$ spectrum from the adhesive failure surface (see Figure 12B) consisted of four components near 284.6, 285.6, 286.3 and 288.9 eV. Identical components were observed in $\text{C}(1s)$ multiplex spectra of the neat adhesive. The peak near 286.3 was associated with carbon singly bonded to oxygen in both the phenyl/oxygen ether of the adhesive and ester of the crosslink. The two bands near 288.9 eV and 285.6 eV were due to carbon triply bonded to oxygen in the ester crosslinks and carbon singly bonded to nitrogen in BDMA, respectively.

The $\text{Cu}(\text{LVV})$ spectra consisted of a single broad band near a kinetic energy of 914.5 eV while the $\text{Cu}(2p_{3/2})$ spectra consisted of a single band near 933.7 eV (see Figure 12B), resulting in a modified Auger parameter of 1848.2 eV. This value was too low to correspond to metallic copper or Cu_2O . Moreover, it was clear that the copper species was not CuO because of the lack of shake-up satellites characteristic of $\text{Cu}(\text{II})$ in the $\text{Cu}(2p_{3/2})$ spectra.

It was tentatively concluded that the copper species present on the adhesive failure surface was the Cu(I) salt of NMA.

The C(1s) spectrum from the adherend failure surface of an aluminum/epoxy MDCB sample (see Figure 13A) consisted of three components near 284.6, 286.3 and 288.7 eV which were all attributed to NMA adsorbed as a carboxylate on aluminum oxide. The modified Auger parameter calculated from the Cu(2p_{3/2}) photoelectron line near 933.9 eV and the Cu(LVV) Auger electron line near 918.0 eV was 1851.9 eV, which was characteristic of CuAl₂ (17). There was no evidence in the Cu(2p_{3/2}) or Cu(LVV) spectra for formation of the copper salt. It was concluded that NMA was adsorbed onto the aluminum oxide and that copper from the alloy was inhibited from interacting with the anhydride curing agent in the adhesive by the oxide which was mostly Al₂O₃.

XPS multiplex spectra obtained from the adhesive failure surface are presented in Figure 13B. The C(1s) spectra consisted of four components near 284.6, 285.6, 286.3 and 288.9 eV which were all characteristic of the cured adhesive as indicated above. There was no evidence of copper on the adhesive failure surface, and failure appeared to be near the adhesive/oxide interface.

The results described above indicate that NMA adsorbs onto the oxidized surfaces of copper and aluminum by dissociation to form carboxylate species. The reaction continues in the case of copper substrates and a layer of carboxylate species is built up in the interphase. However, in the case of aluminum substrates, the reaction does not appear to proceed beyond a monolayer.

In order to characterize the reaction between NMA and copper and 2024 aluminum more carefully, thick films of NMA were applied to polished aluminum and copper mirrors. The mirrors were heated for two hours at 150°C, cooled to room temperature, and rinsed with acetone. RAIR and XPS were then used to examine the films on the mirrors. The infrared spectra obtained from the NMA films deposited on aluminum and copper mirrors were very similar to the spectra obtained from the substrate failure surfaces of aluminum/epoxy and copper/epoxy MDCB specimens (see Figure 14). These results substantiated the assignment of the bands near 1609 and 1460 cm^{-1} in spectra obtained from the substrate failure surfaces of aluminum/epoxy MDCB specimens and those near 1570 and 1420 cm^{-1} in spectra obtained from copper/epoxy MDCB specimens to carboxylate species formed by reaction of NMA with the oxides.

Figure 14C is a transmission infrared spectrum of the copper salt of NMA that was prepared by immersing a copper mirror in a 3% solution of NMA in 2-propanol. After about two weeks, a blue precipitate formed. The infrared spectrum of the precipitate contained two strong absorption bands near 1570 and 1420 cm^{-1} characteristic of the COO^- stretching vibrations of a copper(II) carboxylate similar to those formed on the copper surface after heating under NMA. When an aluminum mirror was immersed in a solution of NMA, no precipitate was formed.

The C(1s) XPS multiplex spectra of NMA films on aluminum and copper substrates (see Figure 15) contained three components, a main peak near 284.6 eV and two smaller peaks near 286.3 eV and 288 eV that were assigned to hydrocarbons, carbon singly bonded

to oxygen, and carbon triply bonded to oxygen, respectively. The highest binding energy C(1s) peak from the copper surface was near 288.1 eV (see Figure 15A) while the peak from the aluminum surface was near 288.7 eV (see Figure 15B). The C(1s) region of the copper/NMA salt contained only two components, the main hydrocarbon peak near 284.6 eV and a higher energy peak near 288.1 eV associated with a metal-carboxylate (see Figure 15C).

The Cu(2p_{3/2}) spectrum from the copper surface (see Figure 15A) consisted of a shoulder near 932.8 eV and a peak near 934.6 eV with two "shake-up" satellite peaks near 939.6 eV and 944.6 eV. Since the Cu(LVV) region contained two component peaks (see Figure 15A), two species of copper were present. The 932.8 eV photoelectron peak combined with the 916.6 eV Auger electron peak produced a modified Auger parameter of 1849.4 eV, which was characteristic of Cu₂O (14,15). The 934.6 eV photoelectron peak together with its two "shake-up" satellites was characteristic of Cu(II). This photoelectron line and the Auger electron peak near 915.5 eV resulted in a modified Auger parameter of 1850.1 eV, which was associated with the copper/NMA salt (see Figure 15C).

A weak peak in the Cu(2p_{3/2}) region of the 2024 aluminum substrate (see Figure 15B) was observed near 934.0 eV, with a corresponding Cu(LVV) Auger peak near 918.0 eV. The modified Auger parameter calculated from these two peaks was 1852.0 eV and was characteristic of CuAl₂. It was apparent that the copper in the alloy did not react with NMA to form a salt, but was present as a precipitate below the oxide.

The $\text{Cu}(2p_{3/2})$ spectra obtained from the precipitate consisted of a band near 934.2 eV plus the satellites characteristic of Cu(II) (see Figure 15C). The corresponding Auger spectra consisted of a single broad band near 915.5 eV, resulting in a modified Auger parameter of 1849.7 eV, which was very close to that observed (1850.1 eV) when NMA films were heated against copper mirrors.

Shake-up satellites were observed in the $\text{Cu}(2p_{3/2})$ spectra of NMA films heated on copper mirrors and of the precipitate formed when copper mirrors were immersed in a solution of NMA (see Figures 15A and 15C), indicating that the copper species was Cu(II) . However, no shake-up satellites were observed in the $\text{Cu}(2p_{3/2})$ spectra obtained from the substrate failure surfaces of copper/epoxy MDCB beam specimens (see Figure 12), indicating that the copper species present on those surfaces was Cu(I) .

It is possible that Cu(II) on the failure surfaces was reduced to Cu(I) during irradiation by x-rays and that reduction was not observed for NMA films on copper or for the precipitate. In fact, Sesselmann (19) has shown that radiation induced reduction was much more pronounced in thin films of CuCl_2 formed on copper substrates than in powdered samples of CuCl_2 .

D. Structure of Metal/Amine-Cured Epoxy Interphases.

Very interesting results were obtained when the fracture surfaces of joints prepared by curing the epoxy/polyamine adhesive against unprimed aluminum were examined by XPS. Figure 16A shows the $\text{N}(1s)$ spectra obtained from the bulk cured adhesive. As expected, the spectra consisted mostly of a band

near 398.0 eV that was attributed to nitrogen atoms that were bonded to carbon and hydrogen. However, a very weak band that was assigned to protonated amino groups was also observed shifted toward higher binding energies by about 2.0 eV. Figure 16B shows the N(1s) spectrum obtained from the epoxy fracture surface. Once again two components were observed but the relative intensity of the component at the highest binding energy was considerably greater. Figure 16C shows the N(1s) spectrum obtained from the corresponding substrate fracture surface. In this case the higher binding energy component accounted for approximately 50 % of the total intensity of the N(1s) band and it was concluded that the composition of the adhesive closest to the substrate surface was much different from that of the bulk adhesive.

It seems likely that acidic hydroxyl groups present on the aluminum surface are capable of protonating the the amino groups in the curing agent, resulting in the relatively strong component near 399.5 eV in the N(1s) spectra obtained from the fracture surfaces. The small band near 399.5 eV in spectra obtained from the bulk adhesive may be related to protonation of some amino groups by hydroxyl groups present in the cured adhesive.

Additional evidence of the difference in molecular structure between the adhesive near the substrate surface and the bulk adhesive was obtained from an analysis of the C(1s) multiplex spectra. As shown in Figure 17, the C(1s) spectra consisted of three components. The strongest, near 284.6 eV, was related to carbon bonded to hydrogen or to carbon. A component shifted

upward in binding energy by about 1.0 eV was assigned to carbon bonded to nitrogen while the component shifted upward by about 1.68 eV was related to carbon making one bond with oxygen.

The components related to C-O and C-N bonds were 8.5 and 32.0 % of the total C(1s) intensity for the bulk adhesive and 11.4 and 28.0 % for the adhesive fracture surface. These results indicate that the extent of cure of the adhesive adjacent to the substrate surface was different from that in the bulk. Reaction between amino and epoxy groups results in the loss of a C-O bond and the formation of a C-N bond. Since the number of C-O bonds was lower at the interface than in the bulk and the number of C-N bonds was higher, it was concluded that the extent of cure was greater at the substrate surface than in the bulk adhesive.

E. Surface-Enhanced Raman Scattering

All of the information regarding interphases that is described above was obtained using XPS, ATR, and RAIR to examine failure surfaces of DCB specimens. It is extremely desirable to develop non-destructive techniques for characterizing polymer interphases on a molecular level but there are few applicable analytical techniques. However, several preliminary experiments have been carried out which indicate that surface-enhanced Raman scattering (SERS) may be useful as a non-destructive probe for determining the structure of interphases in adhesive joints. SERS is a process wherein the Raman scattering from molecules placed adjacent to the roughened surfaces of certain metals, such as copper, silver, and gold, is enhanced as much as six orders of

magnitude. The enhancement for molecules farther away from the metal surface is much lower.

Since normal Raman scattering by polymers is usually quite weak but the enhancement for molecules next to metal surfaces is so great, it was considered that SERS might be used to characterize the interphase between a film of adhesive and a SERS-active substrate without interference from Raman scattering by the bulk of the adhesive as long as the adhesive film was less than about a thousand angstroms in thickness. Once the thickness of the adhesive film exceeds about a thousand angstroms, normal Raman scattering by the bulk of the film becomes comparable in intensity to SERS by molecules adsorbed onto the metal.

We have used SERS to examine the interphase between a model acrylic adhesive and a SERS-active silver substrate. The adhesive consisted of an acrylic monomer and a complex cure system containing saccharin and several other components.

The Raman spectrum of a film of adhesive about a thousand angstroms thick deposited onto a SERS-active silver film (see Figure 18A) was essentially identical to normal Raman spectra of the sodium salt of saccharin (see Figure 18B) and to Raman spectra obtained from thin films of saccharin deposited onto SERS-active silver substrates (see Figure 18C). It was concluded that saccharin from the adhesive was preferentially adsorbed at the silver surface to form a salt.

No bands that could be attributed to normal Raman scattering by the bulk of the adhesive were observed in Figure 18A. These results indicate that SERS can indeed be used for non-destructive

characterization of interphases between polymer films and SERS-active substrates as long as the polymer films are not so thick that normal Raman scattering by the bulk of the films becomes comparable in intensity to the SERS from the interphase. That means the polymer films must be less than approximately 1,000 Å in thickness.

IV. Conclusions

The characteristics of interphases formed when model adhesives were cured against substrates primed with aminosilanes varied depending on the adhesive and the substrate. Copper-containing metal substrates catalyzed the oxidative degradation of aminosilane primers but commercially pure aluminum substrates inhibited the oxidation. When an epoxy/tertiary amine adhesive was cured against a primed substrate, there was little interdiffusion of the adhesive and primer and a sharp interface was obtained between the adhesive and primer. When an epoxy/anhydride adhesive was cured against a primed substrate, there was considerable interdiffusion of the curing agent and the primer and a broad interphase with unique composition was formed.

Complex interphases were also formed when model adhesives were cured against unprimed metal substrates. When an epoxy/polyamine adhesive was cured against unprimed aluminum, the amino groups adjacent to the surface were protonated while those in the bulk of the adhesive were not and the extent of cure of the adhesive was greater at the surface than in the bulk. When an epoxy/anhydride adhesive was cured against unprimed substrates, the anhydride reacted with the oxide to form

carboxylate species. In the case of copper substrates, the oxide was etched and the carboxylates diffused into the adhesive. The anhydride adsorbed onto oxidized aluminum substrates to form a monolayer of surface carboxylates but the oxide was not etched.

Surface-enhanced Raman scattering was used for non-destructive characterization of interphases between polymers and metals, such as copper, silver, and gold, which are SERS-active, as long as the polymer films are not so thick that normal Raman scattering by the bulk of the films is comparable in intensity to SERS from the interphase. When an acrylic adhesive was cured against a silver substrate, results obtained from SERS showed that saccharin and benzoic acid, which were components of the adhesive cure system, segregated to the surface and formed a silver salt.

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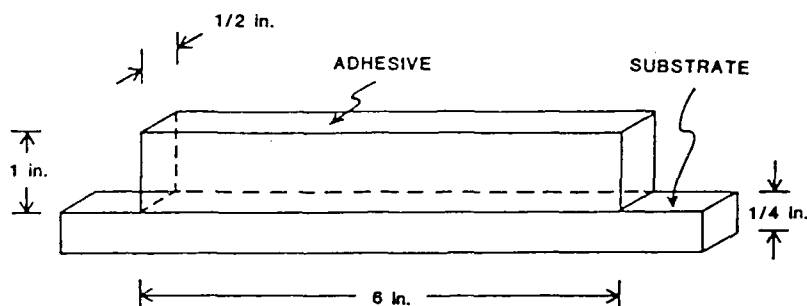


Figure 1. Double cantilever beam test specimen.

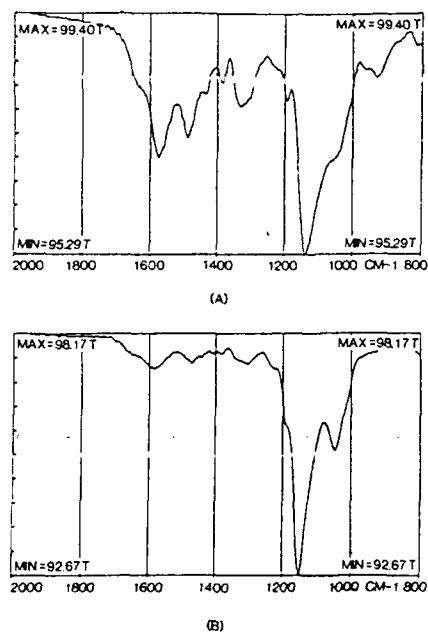
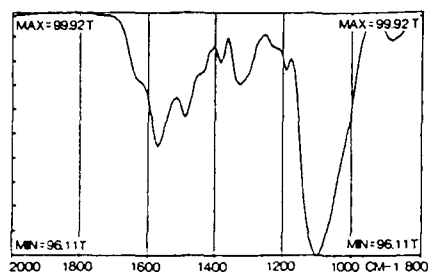
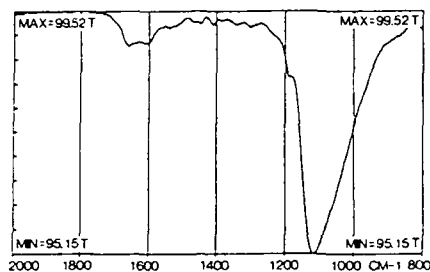


Figure 2. RAIR spectra obtained from polished steel dipped into a 2% aqueous solution of γ -APS for 1 min. and then blown dry with nitrogen: (A)-after curing for 30 minutes at room temperature and (B)-after postcuring for 1 hour at 110°C.



(A)



(B)

Figure 3. RAIR spectra obtained from polished 2024 aluminum dipped into a 2% aqueous solution of γ -APS for 1 min. and then blown dry with nitrogen: (A)-after curing for 30 minutes at room temperature and (B)-after postcuring for 1 hour at 110°C.

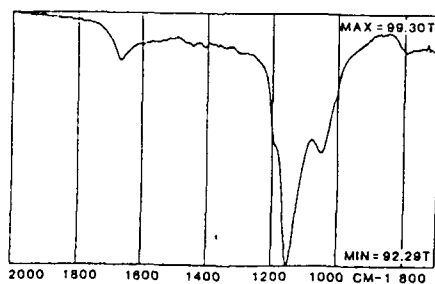


Figure 4. RAIR spectrum obtained from a polished steel mirror dipped into a 2% aqueous solution of γ -APS for 1 min., blown dry with nitrogen, cured at room temperature for 30 min., and postcured at 150°C for 1 hour.

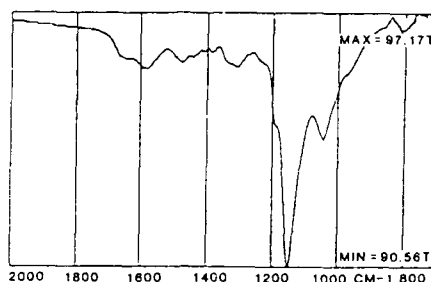


Figure 5. RAIR spectra obtained from polished 1100 aluminum dipped into a 2% aqueous solution of γ -APS for 1 min., blown dry with nitrogen, cured for 30 minutes at room temperature and postcured for 1 hour at 150°C.

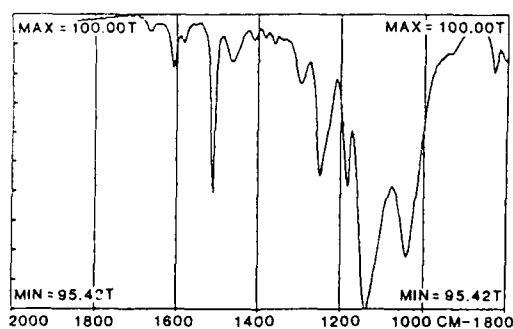


Figure 6. RAIR spectrum obtained from a polished steel mirror that was immersed in an aqueous solution of γ -APS at pH 10.4 for 1 min., dried at room temperature for 30 min., reacted with epoxy at 150°C for 1 hour, and rinsed with MEK.

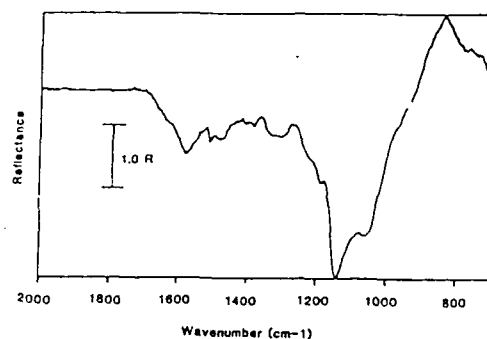


Figure 7. RAIR infrared spectrum of the substrate failure surface of a DCB specimen prepared from a steel substrate and an epoxy cured at 75°C for one hour with a tertiary amine. The substrate was primed with a dilute aqueous solution of γ -APS.

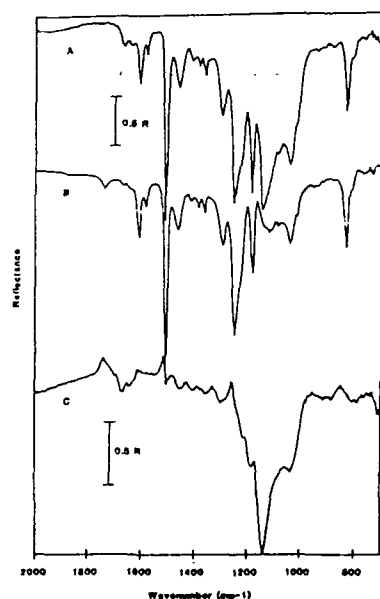


Figure 8. RAIR spectra of (A) - the failure surface of a DCB prepared from a steel substrate primed with γ -APS and an epoxy cured with a tertiary amine curing agent, (B) - a film of the same epoxy deposited on a polished steel substrate, and (C) - the difference of A and B. In A and B the epoxy was cured at 150°C for one hour.

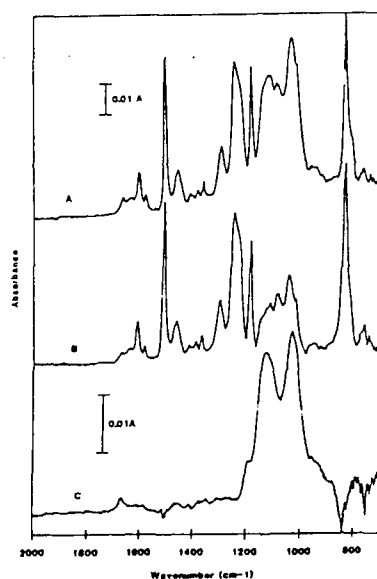


Figure 9. ATR infrared spectra of the adhesive failure surfaces of DCB specimens prepared from steel substrates and the epoxy cured with a tertiary amine at 150°C for one hour; (A) - substrate primed with a dilute aqueous solution of γ -APS, (B) - substrate unprimed, and (C) - the difference of A and B.

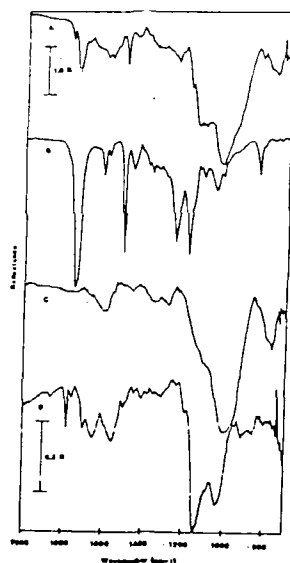


Figure 10. RAIR spectra obtained from (A) - the substrate failure surface of a DCB specimen prepared by curing a beam of the epoxy/anhydride at 150°C for two hours against a 2024 aluminum beam primed with γ -APS, (B) - a thin film of the epoxy/anhydride applied to a 2024 aluminum mirror and cured, (C) - the substrate failure surface of a DCB specimen that was cured against an unprimed 2024 aluminum beam, and (D) - the difference of A, B, and C.

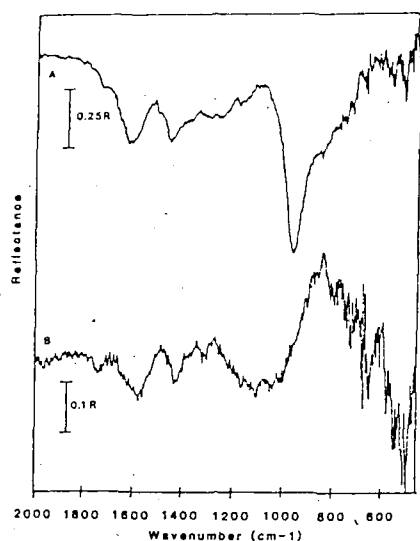


Figure 11. RAIR spectra obtained from the adherend failure surfaces of (A)-aluminum/epoxy and (B)-copper/epoxy MDCB specimens cured for 24 hours at 150°C.

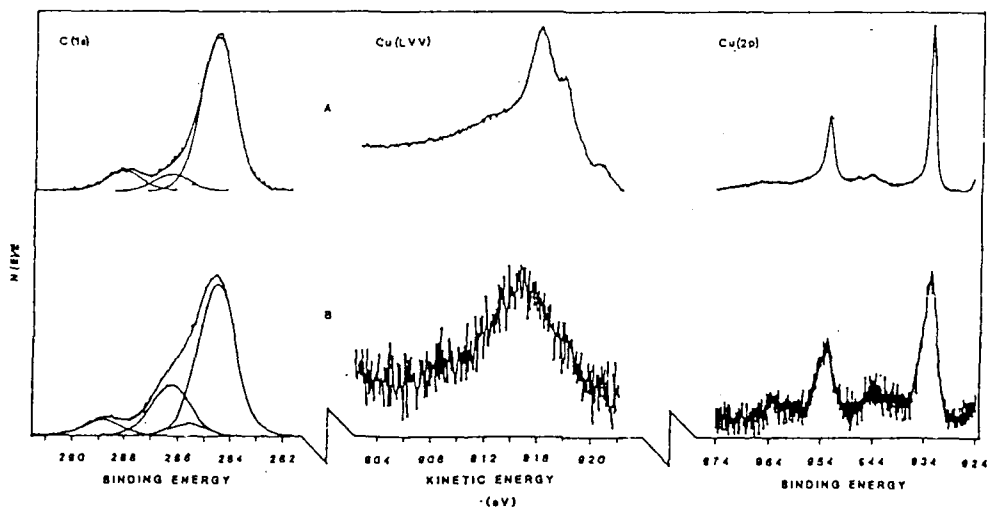


Figure 12. XPS multiplex spectra of the (A)-adherend and (B)-adhesive failure surfaces of a copper/epoxy MDCB specimen cured for 24 hours at 150°C.

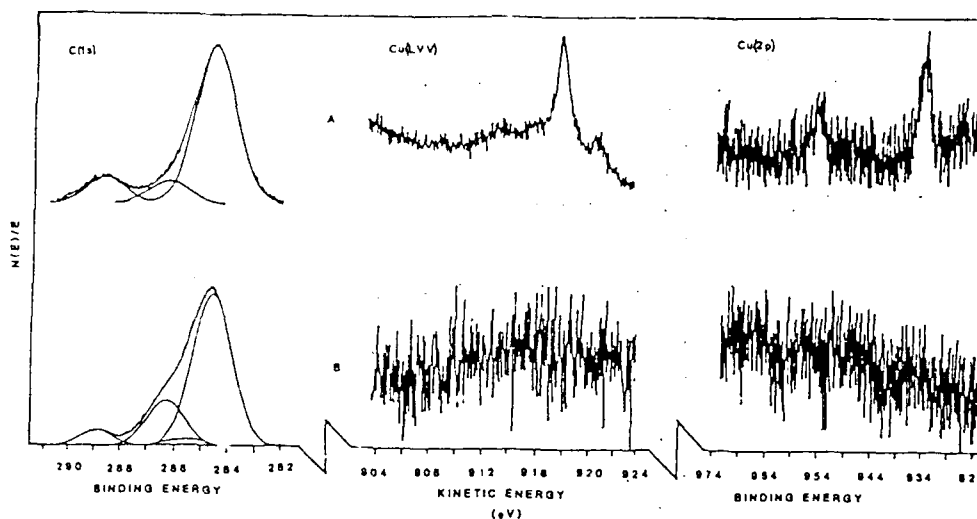


Figure 13. XPS multiplex spectra of the (A)-adherend and (B)-adhesive failure surfaces of an aluminum/epoxy MDCB specimen cured for 24 hours at 150°C.

Figure 14. RAIR spectra obtained after thick films of NMA were applied to (A)-copper and (B)-2024 aluminum substrates, heated for 2 hours at 150°C, cooled to room temperature, and rinsed with acetone. Spectrum (C) is a transmission infrared spectrum of the copper salt of NMA formed by immersing a copper foil in a 3% solution of NMA in isopropanol.

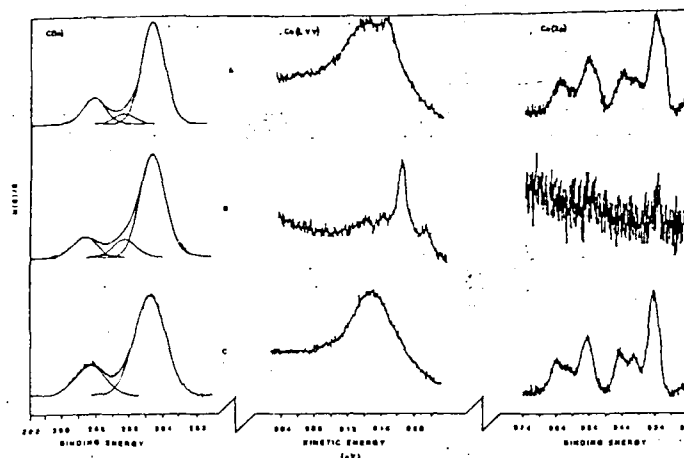


Figure 15. XPS multiplex spectra obtained after thick films of NMA were applied to (A)-copper and (B)-2024 aluminum substrates, heated for 2 hours at 150°C, cooled to room temperature, and rinsed with acetone. XPS multiplex spectra of the copper salt of NMA formed by immersing a copper foil in a 3% solution of NMA in isopropanol are shown in (C).

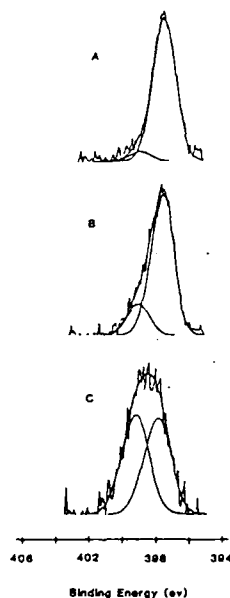


Figure 16. XPS N(1s) multiplex spectra obtained from (A)-the bulk adhesive, (B)-the adhesive fracture surface, and (C)-the adherend fracture surface after an epoxy/polyamine was cured against an aluminum substrate.

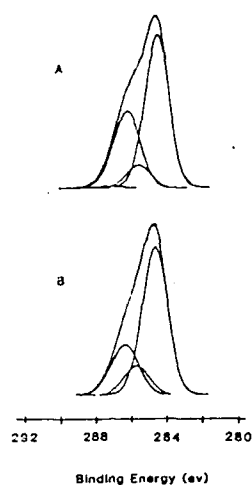


Figure 17. C(1s) multiplex spectra obtained from (A)-the cured bulk adhesive and (B)-the adhesive fracture surface after an epoxy/polyamine was cured against an aluminum substrate.

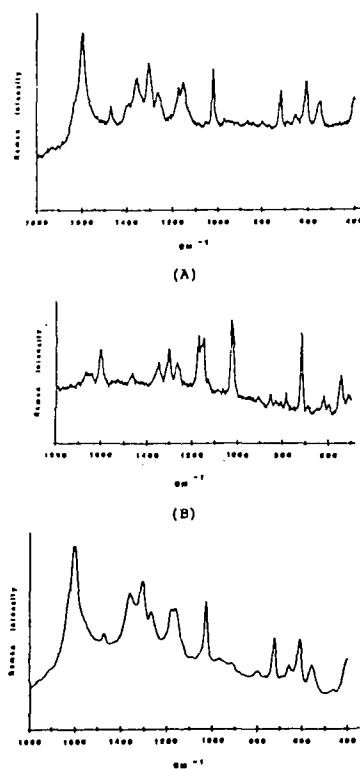


Figure 18. (A) - Surface-enhanced Raman scattering from a thick film of acrylic adhesive deposited onto a silver substrate, (B) - normal Raman scattering from the sodium salt of saccharin, and (C) - SERS from a thin film of saccharin deposited on silver.

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University of Illinois
Urbana, IL 61801

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University of Cincinnati
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Martin Marietta Laboratories
1450 South Rolling Road
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